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PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Process for Neutralising Acidic Acetone-phenol Mixtures

We, SOCIETA' ITALIANA RESINE, an Italian body corporate, of 33, via Grazioli, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known that acidic cleavage or hydrolysis of pure or dilute cumene hydroperoxide yields phenol and acetone. The acidic cleavage reagents employed in the hydrolysis or cleavage are normally non-oxidising inorganic acids, such as sulphuric and/or hydrochloric acid, the cleavage usually being performed on an "oxidate" containing from 20 to 90% by weight cumene hydroperoxide, the balance consisting essentially of cumene and its decomposition products formed during the oxidising reaction, such as acetophenone and dimethyl or phenylcarbinol.

While still acidic the hydrolysis mixtures cannot be conveyed to the subsequent rectifying columns, for the free acid therein would give rise to serious corrosion problems.

Neutralisation of the acidic hydrolysis mixtures of cumene hydroperoxide is normally effected by means of caustic soda, sodium carbonate or sodium phenolate solutions.

The acid employed for hydrolysis of cumene hydroperoxide is effectively neutralized in this manner, but, at the same time, serious drawbacks arise in the subsequent fractionations for recovery of phenol and acetone.

The inorganic salts formed, such as sodium sulphate, remaining in the neutralised mixture tend to separate, thereby obstructing lines, and choking reboilers, while sodium salts of the carboxylic acids contained in the cumene hydroperoxide solution decompose under the action of heat during distillation and the resulting by-products contaminate more particularly the acetone which does not meet therefore the standard purity tests.

In order to obviate in part at least the above drawbacks it was suggested to separate from the neutralised hydrolysis mixture a fraction containing most of said alkali metal salts and to wash the mixture with pure water.

While washing removes in part at least the abovementioned difficulties, it entails a considerable loss of acetone and phenol which dissolve in the washing water and can only be recovered with difficulty, which is more particularly true of phenol on account of the low concentrations and characteristics of the phenol water distillation curve. This necessitates elaborate solvent-extraction processes.

This invention provides a novel method of neutralising acidic mixtures produced by the acidic hydrolysis of an oxidate containing at least 25% by weight cumene hydroperoxide whether side-products of oxidation of cumene air or molecular oxygen, such as acetophenone and dimethylphenylcarbinol are present or not, by simply causing the mixture to flow over anion-exchange resin of the anion type. The resin is advantageously contained in a suitable column.

It is surprising that sulphuric acid and other inorganic acids used for the acidic cleavage of oxidates containing at least 25% by weight cumene hydroperoxide can be thoroughly removed over anion exchange resins from substantially non-aqueous solutions in the presence of phenol.

The advantages afforded by the above procedure can be summarized as follows:

1) total absence in the effluent from the neutralising plant of inorganic or organic alkali and alkaline-earth salts which could settle-out in the reboilers in the rectification columns;

2) the water content in the effluent is not increased with respect to supply, which is of a considerable advantage in the rectification of the various products therein contained;

3) valuable products, such as acetone and

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phenol contained in the hydrolysis mixture are wholly retained by the effluent.

The reaction mechanism is:

(absorption) $nR-OH + A \cdot H_2 \rightarrow R_nA + nH_2O$

5 (regeneration) $R_nA + nB-OH \rightarrow nR-OH + B \cdot A$

as is known in the art.

Conventional anion exchange resins are suitable for neutralising the solutions from the hydrolysis of cumene hydroperoxide according to this invention.

Phenolic-base resins having secondary-amino and tertiary-amino functional groups are preferred. Examples of such resins are "Duolite" A7 and "Duolite" A2 manufactured by Chemical Process Co., Redwood City, California, or other resins of similar properties "Duolite" is a trade mark).

Before supply of the acidic liquid to be neutralised is started, the resin should be brought to its hydroxide form by a conditioning treatment with dilute caustic soda solution, whereupon excess caustic soda is removed by means of distilled or demineralized water and residual water in the resin is washed out with acetone until the water has been completely displaced. A fixed bed of resin in a column is advantageously employed.

30 The acetone in the dilute aqueous solution resulting from the above washing is recovered by distillation for re-use.

In industrial practice the dilute acetone solution is conveyed to the purifying column in which the raw acetone recovered from the hydrolysis mixture is also purified.

When the water has been fully displaced from the resin the acetone supply is stopped and the supply of the acidic hydrolysate to be neutralised is started.

When the resin is spent, the supply of the acidic hydrolysate is stopped, and the residual partly-neutralised hydrolysate in the resin is displaced by acetone, the resulting mixture being added to the acidic hydrolysate to be neutralised in the next run.

Upon completion of the above displacement, the acetone is displaced in turn by demineralized or distilled water, the resulting dilute acetone being added to the dilute acetone previously obtained during the resin-conditioning step.

At this stage conventional regeneration of the resin by means of a sodium hydroxide solution is effected, whereupon the cycle is repeated.

The above described working cycle can be modified as follows.

60 Upon washing the resin bed with water after regeneration with caustic soda, instead of displacing the residual water in the resin with acetone as described above, the water is discharged from the resin bed simply by draining.

65 Water absorbed by the resin is removed

by a warm air stream at a temperature which will not damage the resin, this temperature generally does not exceed 45—50° C.

When the moisture content in the air at the outlet is identical to that at the air inlet the resin is sufficiently dehydrated; the air supply is stopped and supply of the mixture to be neutralised is started.

Upon completion of the cycle instead of displacing the residual semi-neutralised mixture in the resin by means of acetone as previously described, the mixture is drained from the neutralization column with the assistance of compressed air for improving exhaustion and purging the bed.

Upon discharge of the mixture, an acetone quantity slightly exceeding the volume of the resin is introduced three times into the column from the bottom of the latter, the washing acetone being discharged in each instance from the bottom of the column.

Upon completion of the last washing step by means of acetone, a similar volume of demineralized or distilled water is supplied from the bottom.

The aqueous acetone solution formed is likewise discharged from the bottom and conveyed to the acetone distillation apparatus mentioned above.

Water-washing and regeneration steps are thereafter effected.

The enclosed drawing diagrammatically shows an apparatus for carrying out this invention.

The apparatus comprises a column 10 the lower half of which contains a bed 11 of anion-exchange resin.

The bed is supported on a porous septum 14 and a further porous septum 12 is arranged between the bed and the top of the column.

Tanks 15 and 16 are arranged above the column and connect with a top section of the latter through conduits 17, 18, respectively, equipped with control valves 19, 20, respectively.

In operation, tank 15 contains a sodium hydroxide solution, whereas acidic hydrolysate is contained in the tank 16.

Demineralized or distilled water can be supplied to the column either through a conduit 21 equipped with a control valve 22 opening into the top section of the column, or through a conduit 21a equipped with a control valve 22a opening into the bottom section of the column beneath porous septum 14.

Further two conduits, denoted by 23 and 24 open into the top section of the column via control 25, 26, respectively, for supplying to the column acetone and warm air (45°—50° C) respectively.

A discharge conduit 28 ending by a three-way valve 29 extends from the bottom of the column, the valve 29 being adapted to selec-

displaced by means of an air stream at 45° C.

When the moisture content in the outflowing air is equal to that in the in-flowing air, the air supply is stopped and the hydrolysate solution is caused to flow downwardly at a rate of 0.7 liters/hour.

The resin is exhausted after 30 hours.

The column is emptied through valve 29 and conduit 32 with the assistance of compressed air, the discharged mixture being recycled through conduit 35.

Acetone is then caused to flow in upward flow at a rate of 0.7 liters/hour during 30 minutes, then discharged from the bottom.

This step is repeated three times totalling about 1.1 liters acetone.

Upon discharge of the acetone of the last washing, water is caused to flow in upward flow (counter-current) at a rate of 0.7 liters/hour for 20 minutes.

The aqueous acetone solution containing 40% by weight acetone is discharged from the bottom via conduit 30 and conveyed to acetone-recovery apparatus.

The resin is then regenerated as in Example 1 for a subsequent run.

EXAMPLE 3

A "Duolite" A2 exchange resin is used. The steps are carried out as described in Example 1. The resin becomes exhausted after 24 hours instead of 29 hours on account of the lower exchange capacity of A2 resin with respect to the A7 grade.

EXAMPLE 4

"Duolite" A2 exchange resin is used similarly to Example 3.

The same steps as described in Example 2 are carried out.

The resin becomes exhausted after 25 hours instead of 30 hours for the reason explained in Example 3.

WHAT WE CLAIM IS:—

1. A method of neutralising the phenol and acetone-containing acidic hydrolysate obtained by the hydrolysis of solutions of cumene hydroperoxide in cumene containing at least 25% by weight of cumene hydroperoxide, with inorganic acids, which comprises passing the acidic hydrolysate in contact with an anion exchange resin.

2. A process according to claim 1 in which the resin is arranged in a fixed bed and the hydrolysate is contacted with the resin by causing the hydrolysate to flow through the bed until the exchange capacity of the resin is nearly or completely exhausted and the resin is then regenerated by means of an alkali-metal hydroxide solution.

3. A process according to claim 2, in which the nearly or completely exhausted resin is first purged with acetone, then washed with demineralised water, and then regenerated with the alkali-metal hydroxide solution.

4. A process according to claim 2 in which the nearly or completely exhausted resin is purged with air and then repeatedly flooded with acetone, the acetone is then displaced from the bed by means of demineralised water and the resin in the bed is then regenerated by the alkali metal hydroxide solution.

5. A process according to any of claims 2 to 4 in which the regenerating solution is displaced from the resin bed first by demineralised water and then by air or acetone.

6. A process for neutralising a hydrolysate obtained by the hydrolysis with inorganic acids of a solution of cumene hydroperoxide in cumene containing at least 25% by weight cumene hydroperoxide, substantially as herein described in any of the Examples.

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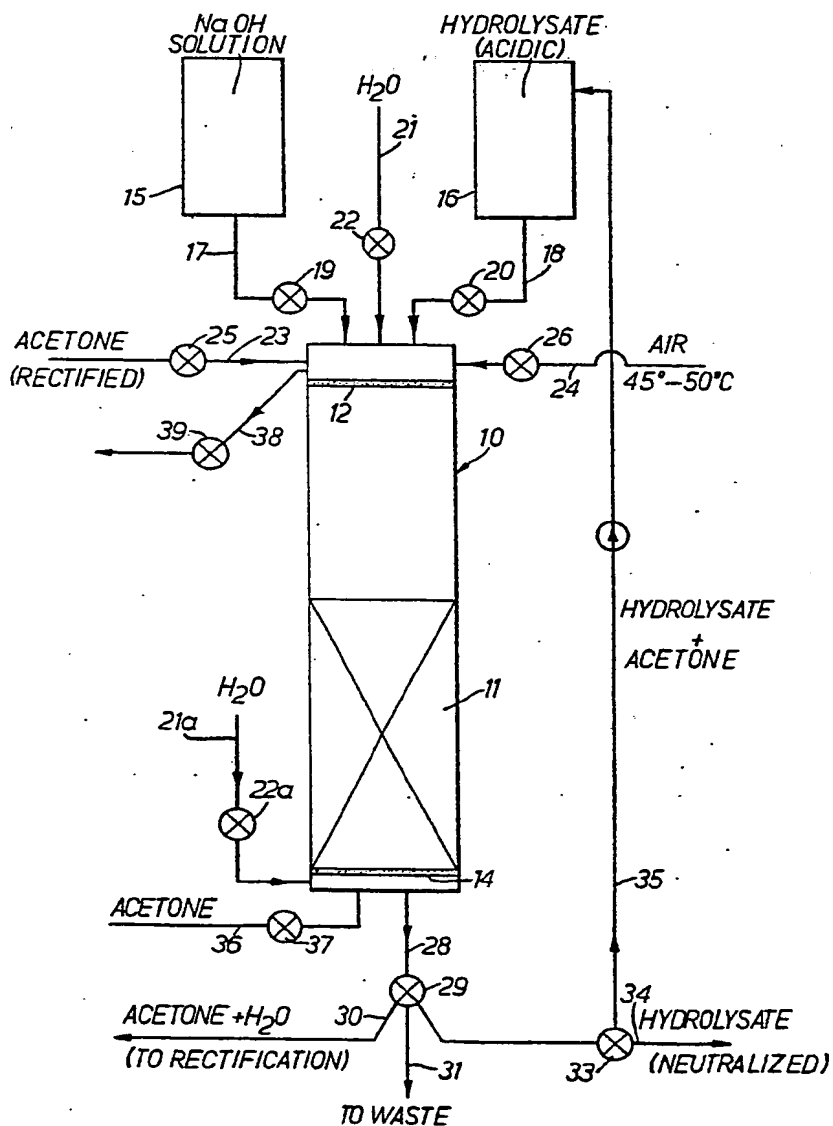
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COMPLETE SPECIFICATION

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